OPIC
OFFICE DE LA PROPRIÉTÉ INTELLECTUELLE DU CANADA

CIPO
CANADIAN INTELLECTUAL PROPERTY OFFICE

(12) (19) (CA) **Brevet-Patent**

(11) (21) (C) **2,097,218**
(22) 1993/05/28
(43) 1993/12/17
(45) 1999/10/05

(72) Gumy, Didier, CH
(72) Wursch, Pierre, CH
(73) SOCIETE DES PRODUITS NESTLE S.A., CH

(51) Int.Cl.[6] C12P 19/14, A23L 1/0522
(30) 1992/06/16 (1896/92-9) CH

(54) **PROCEDE DE PRODUCTION D'UN PRODUIT AMYLACE STABLE APPARENTE A LA CIRE ET PRODUIT AINSI OBTENU**

(54) **PROCESS FOR THE PRODUCTION OF A STABLE WAX-LIKE AMYLACEOUS PRODUCT AND THE PRODUCT OBTAINED**

(57) The invention provides a process for stabilizing a native waxy amylaceous product containing at least 95% by weight of amylopectin based on the total weight of dry product, which comprises providing an aqueous suspension containing 5-30% by weight of the amylaceous product, heat treating the suspension at a temperature of 65-75°C in order to form a gelatinized amylaceous product and forming a hydrolysed product by subjecting the gelatinized product to hydrolysis with a pure .beta.-amylase so as to obtain a degree of hydrolysis of between 5% and 20%. The stable native waxy amylaceous product so produced is suitable for use in food products and provides improved texture and stability during storage.

2097218

This invention relates to a new stable amylaceous product and to a process for its production.

All starches, except for waxy types, contain two polymers of glucose, namely amylose and amylopectin. When a non-waxy starch suspension is heat-treated, the starch granule obtained swells irreversibly and the amylose is preferentially solubilized. During cooling of the suspension, the amylaceous polysaccharides undergo retrogradation, rapidly in the case of amylose (i.e. in a few hours) and more slowly in the case of amylopectin (over a few days). This retrogradation particularly affects the texture of foods containing these starches and makes them unacceptable.

Accordingly, it is preferable to use an amylaceous product rich in amylopectin, such as a waxy cornstarch. However, the stability of the gels and binders obtained from amylaceous products rich in amylopectin is not sufficient for the needs of the food industry where a keeping time of several months is occasionally necessary.

It is known that inter alia the stability of the gels thus obtained in storage can be improved, for example, by treating the amylaceous product to be used in such a way that the amylopectin molecule is chemically modified. For example, a few glucose units may be replaced by hydrophilic or hydrophobic organic molecules or by a mineral anion which enables the amylopectin molecule to be stabilized and the risk of retrogradation to be reduced.

It is also possible to form organic or mineral diester bridges or diethers between two glucose units belonging to two different chains. This crosslinking

enables the swelling which the starch granule undergoes during the heat treatment to be reduced and hence the rheological characteristics of the amylopectin molecule to be modified, making it more resistant to the mechanical treatments (shearing) and to the acidic medium. These chemical modifications provide the amylopectin gels obtained with various desirable physical properties, such as high gelling power and high stability in neutral and/or acidic medium, for example during cooking, sterilization or deep-freezing treatments. However, the stable amylaceous products obtained have the disadvantage of having been chemically treated which may not be well received by consumers.

The problem addressed by the present invention was to obviate the disadvantage mentioned above by providing a process for the production of a stable amylaceous product involving only a controlled hydrolysis reaction, but no chemical treatment as such.

Accordingly, the present invention relates to a process in which a native waxy amylaceous product is gelatinized and then hydrolyzed with a pure β-amylase.

The present invention also relates to the stable native waxy amylaceous product obtained by this process.

One advantage of the invention is that it provides a process which is simple and easy to carry out on an industrial scale and which gives a stable product in the form of a gel. In the context of the invention, a stable product is understood to be a product which, above all, is stable during storage, i.e. does not undergo any syneresis or change in viscosity as a function of time, but which is also stable to freezing/defrosting. Another advantage of the process according to the invention is that it gives an end product which may be used, for example, as a so-called instant binder in refrigerated or deep-frozen products.

In the context of the invention, a waxy amylaceous product is understood to be a flour or a starch of an amylaceous product or of a mixture of amylaceous products, such as cereals, which are particularly rich in amylopectin, i.e. contain at least 95% by weight thereof, based on the total dry weight of starch. Examples of waxy amylaceous products particularly corresponding to the invention are waxy cornstarch or flour, waxy rice starch or flour and waxy barley starch or flour. A native amylaceous product is understood to be a product which has not been chemically modified.

In a first step of the process according to the invention, the amylaceous product is gelatinized. The gelatinization step may be carried out, for example, by heat treatment of an aqueous suspension containing 5 to 30% by weight of the amylaceous product for 8 to 12 minutes at a temperature of 65 to 75°C. During this step, the starch granules swell to allow subsequent enzymatic hydrolysis. The gelatinized amylaceous product is then enzymatically hydrolyzed with a pure ß-amylase of vegetable or bacterial origin. To this end, the ß-amylase may be added in the form of an aqueous solution in a quantity of 500 to 6000 U per kg starting starch. The unit U is defined as follows: 1 U corresponds to 1 mg of maltose released in 3 minutes at 20°C/pH 4.8.

The hydrolysis is preferably carried out over a period of 5 to 60 minutes at a temperature of 65 to 75°C and at a pH of 5.6 to obtain a degree of hydrolysis of at least 5%, as measured by chemical determination of the reducing sugars (maltose formed). The reaction in question may also be carried out continuously, for example by heating the aqueous suspension to a temperature of 50 to 60°C at pH 5.6, adding the enzyme, continuing the heat treatment to a temperature of 65 to

75°C and maintaining that temperature for about 5 to 60 minutes to obtain a degree of hydrolysis of at least 5%.

It has surprisingly been found that a degree of hydrolysis of only 5% was sufficient to enable a stable end product to be obtained. The preferred degree of hydrolysis is of the order of 7 to 20%. Although it is possible to go to at least as far as 55%, this does involve a greater loss of end product and hence a reduction in yield.

The hydrolysis has to be carried out with a pure ß-amylase because the presence of α-amylase during the hydrolysis would result in an undesirable reduction in the viscosity of the starch paste obtained.

In addition, it has found that hydrolysis with a ß-amylase enables the size of the amylopectin molecules to be reduced while leaving their branched structure intact so that the viscosity of the gels subsequently obtained can be increased for a constant concentration by weight of amylopectin.

Once the desired degree of hydrolysis has been reached, the enzyme may be inactivated, for example by heat treatment for 8 to 12 minutes at a temperature of 80 to 85°C, for example by injection of steam into the double jacket of the reactor. During this step, it is possible to observe the final swelling of the starch granule and the total development of the viscosity of the end product.

The product thus obtained may then be dried, for example by passage over cylinders rotating at 1 to 3 revolutions per minute and at a temperature of 130 to 160°C, to obtain a precooked amylaceous product having a dry matter content of approximately 95 to 98% by weight. The drying step may also be carried out by spray drying.

The hydrolyzed product obtained may also be

directly used as such, i.e. in moist form, without having to be subjected to a drying step.

The native waxy amylaceous product thus obtained has been hydrolyzed to a degree of at least 5% with a pure ß-amylase and is stable to the extent that it is capable of withstanding several freezing-defrosting cycles without any reduction in its stability and without any change in its viscosity. This amylaceous product may be reconstituted in the cold state and may be used, for example, in sterilized or deep-frozen sauces or in sterilized milk-based desserts.

The invention is illustrated in more detail in the following Examples in which parts and percentages are by weight.

Example 1

An aqueous suspension containing 40 kg waxy cornstarch and 335 litres water is prepared and then heated for about 10 minutes at 70°C to gelatinize the starch. The pH is adjusted to 5.6 with concentrated acetic acid. The temperature is lowered to 55°C. 10 g pure soya ß-amylase (activity 4040 U/g) diluted in 20 litres water are then added and hydrolysis is left to take place over a period of about 60 minutes to obtain a degree of hydrolysis of approximately 13%. When the degree of hydrolysis is reached, the enzyme is inactivated by heat treatment at 80°C, after which the product obtained is dried at 180°C on cylinders rotating at 8 revolutions per minute. The end product obtained has a dry matter content of 97.5% and is in the form of flakes.

A starch paste can be prepared from the product thus obtained by mixing 50 g of the powder-form product in 950 ml water at 25°C. The gel obtained has a glutinous texture comparable with that of the fresh waxy

corn gel.

Measurement of the viscosity of the gel obtained with a Carrimed* instrument gives the following results:

- without shearing: 167 mPas
- after heating (70°C) without shearing: 130 mPas
- after homogenization (Polytron*): 95 mPas
- after heating (70°C) and homogenization: 82 mPas

Example 2

The object of this Example is to determine the effect of the degree of hydrolysis on the stability of the gel obtained and the enthalpy of retrogradation of the amylopectin. A waxy cornstarch is gelatinized, hydrolyzed and dried in the same way as described in Example 1, the degree of hydrolysis being varied.

A starch paste is then prepared by preparation of a mixture containing 20 g of the amylaceous product obtained in 980 ml water. The starch paste thus prepared is then subjected to 1, 3 or 5 freezing/defrosting cycles (one cycle consisting of freezing to -40°C for at least 20 minutes followed by defrosting to ambient temperature) and the volume of water exuded after centrifugation of the defrosted paste is determined.

The following results in % water exuded are obtained:

	Number of cycles			
Degree of hydrolysis	0	1	3	5
0%	0	4	18	27
4.8%	0	0	0	0
5.8%	0	0	0	0
8.1%	0	0	0	0
9.2%	0	0	0	0
12.6%	0	0	0	0

*Trade-mark

A

It can be seen that the hydrolysis step enables the product to be stabilized because the product does not exude water if it has been hydrolyzed, even to a low degree.

A starch paste is then prepared by mixing 400 g amylaceous product in 600 ml water. The enthalpy of retrogradation of the amylopectin is measured after storage for 18 days at 20°C using a Mettler DSC 30* differential calorimeter.

The following results are obtained:

Degree of hydrolysis (%)	0	4.8	5.8	8.1	9.2	12.6
Enthalpy (J/g)	9.6	7.0	4.5	2.9	2.0	0.8

Accordingly, it can be seen that the hydrolysis step enables the rate of retrogradation of the product to be reduced, as reflected in the reduction in enthalpy in dependence upon the degree of hydrolysis.

Example 3

The object of this Example is to determine the effect of the degree of hydrolysis on the stability of the gel obtained and the enthalpy of retrogradation of the amylopectin. A waxy cornstarch is gelatinized, hydrolyzed and dried in the same way as described in Example 1, the degree of hydrolysis being varied.

A starch paste is then prepared by preparation of a mixture containing 400 g of the amylaceous product obtained in 600 ml water. The starch paste thus prepared is then subjected to 1, 3 or 5 freezing/defrosting cycles (one cycle consisting of freezing to -40°C followed by defrosting to ambient temperature) and the enthalpy of retrogradation of the amylopectin is measured under the same conditions as in Example 2.

The following results in J/g are obtained:

*Trade-mark

A

Degree of hydrolysis	Number of cycles 0	1	3	5
0%	0	0	2.4	3.1
1.8%	0	0	0.3	1.0
7.9%	0	0	0.3	0.6
15.8%	0	0	0.4	0.8
36.1%	0	0	0.6	0.7

It can be seen that the hydrolysis step enables the product to be stabilized because the enthalpy of retrogradation becomes very low, even after several freezing/defrosting cycles.

Example 4

An aqueous suspension containing 290 g waxy rice flour and 1650 ml water is prepared and heated for about 10 minutes to 70°C to gelatinize the starch. The pH is adjusted to 5.6 by addition of concentrated acetic acid. The temperature is then lowered to 55°C.

0.05 g pure soya ß-amylase (activity 4040 U/g enzyme) is then added and hydrolysis is left to take place for about 60 minutes to obtain a degree of hydrolysis of 10%. When the degree of hydrolysis is reached, the enzyme is inactivated by heating to 80°C and the starch paste obtained is dried. The end product obtained has a dry matter content of 92% and is present in powder form.

A starch paste may be prepared by mixing 20 g of the product thus obtained with 980 ml water. The starch paste thus prepared is then subjected to 1, 3 or 5 freezing/defrosting cycles and the volume of water exuded after centrifugation of the defrosted starch paste is determined.

The following results in % water exuded are

obtained:

	Number of cycles			
Degree of hydrolysis	0	1	3	5
0%	61	58	56	49
9.8%	0	0	0	0

Accordingly, a product according to the invention can also be prepared from a waxy rice.

Example 5

This Example illustrates the continuous application of the process according to the invention.

An aqueous suspension containing 50 kg waxy cornstarch, 230 litres water and 24.5 g pure soya ß-amylase is prepared and heated to 70°C by injection of steam. Hydrolysis is then left to take place for about 60 minutes at 70°C to obtain a degree of hydrolysis of 7%. When this degree of hydrolysis is reached, the enzyme is inactivated by heating to 80°C. The product obtained has a dry matter content of 18% and may be directly used. The product obtained may also be dried at 180°C on cylinders rotating at 8 revolutions per minute to obtain an end product in the form of flakes having a dry matter content of 95%.

Example 6

This Example illustrates the use of the product according to the invention in a more complete recipe.

A tomato sauce is prepared from tomato concentrate, cream containing 35% fats, spices, salt and approx. 5% of the amylaceous product according to the invention, the amylaceous product having been prepared from cornstarch, hydrolyzed in accordance with the

invention and having a degree of hydrolysis of 8.1%. A sauce containing an amylaceous product based on cornstarch which has not been hydrolyzed is prepared for comparison. The sauces thus prepared are cooked for 10 minutes, placed in a bag, frozen and kept in a refrigerator for 1 week at -18°C. Thereafter, the sauces are heated on a water bath to approximately 60°C.

The following results are obtained:

Sauce according to the invention:

- stable to freezing/defrosting (no water exuded)
- smooth and creamy appearance

Comparison sauce:

- unstable to freezing/defrosting (water exuded)
- contains lumps.

It can be seen that the sauce prepared with the amylaceous product according to the invention is stable in contrast to the comparison sauce.

CLAIMS

1. A process for stabilizing a native waxy amylaceous product containing at least 95% by weight of amylopectin based on the total weight of dry product, which comprises providing an aqueous suspension containing 5-30% by weight of said amylaceous product, heat treating said suspension at a temperature of 65-75°C in order to form a gelatinized amylaceous product and forming a hydrolysed product by subjecting the gelatinized product to hydrolysis with a pure β-amylase so as to obtain a degree of hydrolysis of between 5% and 20%.

2. A process according to claim 1 wherein said β-amylase is of vegetable or bacterial origin.

3. A process according to claim 1 or 2 which further comprises inactivating the β-amylase following hydrolysis by heat treatment at a temperature of 80-85°C.

4. A process according to any of claims 1 to 3 which further comprises drying said hydrolysed product to provide a dry matter content of 95-98% by weight.

5. A stable waxy amylaceous product produced by the process of any of claims 1 to 4.

ABSTRACT

The invention provides a process for stabilizing a native waxy amylaceous product containing at least 95% by weight of amylopectin based on the total weight of dry product, which comprises providing an aqueous suspension containing 5-30% by weight of the amylaceous product, heat treating the suspension at a temperature of 65-75°C in order to form a gelatinized amylaceous product and forming a hydrolysed product by subjecting the gelatinized product to hydrolysis with a pure β-amylase so as to obtain a degree of hydrolysis of between 5% and 20%. The stable native waxy amylaceous product so produced is suitable for use in food products and provides improved texture and stability during storage.